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Comparison of ammonia plasma and AlN passivation by plasma-enhanced atomic layer deposition

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Surface passivation of GaAs by ammonia plasma and AlN fabricated by plasma-enhanced atomic layer deposition are compared. It is shown that the deposition temperature can be reduced to 150 °C and effective passivation is still achieved. Samples passivated by AlN fabricated at 150 °C show four times higher photoluminescence intensity and longer time-resolved photoluminescence lifetime than ammonia plasma passivated samples. The passivation effect is shown to last for months. The dependence of charge carrier lifetime and integrated photoluminescence intensity on AlN layer thickness is studied using an exponential model to describe the tunneling probability from the near-surface quantum well to the GaAs surface. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3694798]

I. INTRODUCTION

The high surface state density of GaAs has necessitated the development of novel passivation methods. GaAs based devices like laser Bragg mirrors, metal-oxide-semiconductor (MOS) structures, and MOS field effect transistors (MOSFET) require effective surface passivation for high performance. Especially the MOSFET has recently raised a lot of interest as an alternative for their silicon based counterparts. AlN is a promising material candidate for passivation of GaAs surfaces at low temperatures (<200 °C), and good performance has recently been demonstrated using AlN layers deposited by sputtering.[1]

A while ago, surface passivation by ultra-thin AlN layers fabricated by plasma-enhanced atomic layer deposition (PEALD) was introduced.[2] The deposition temperature was 200 °C, and contrary to the method mentioned above, no pre-treatment of the GaAs surface is required prior to AlN deposition. This kind of self-cleaning effect due to native oxide removal by the trimethylaluminum (TMA) precursor has already been shown with Al_2O_3 deposited by ALD.[3] In addition, the AlN layers fabricated by PEALD are very hydrogen-rich,[4] and hydrogen has been shown to be a key element in plasma based passivation methods.[5] Other advantages of ALD based methods include conformality, the possibility to cover large surface areas, and the low fabrication temperature.

This paper shows that it is possible to reduce the deposition temperature of PEALD AlN even further down to 150 °C and still passivate GaAs surfaces effectively. The effectiveness is verified by characterizing near-surface quantum well (NSQW) structures by photoluminescence (PL) and time-resolved photoluminescence (TRPL) methods, and by comparing the results with those obtained from samples with AlN layers fabricated at higher temperatures. Furthermore, the passivation by AlN is compared with passivation by pure ammonia plasma. Samples passivated by the former are shown to exhibit several times higher PL intensities and longer charge carrier lifetimes than the latter. The experimentally derived dependence of PL intensity and charge carrier lifetime on AlN layer thickness is explained by a model that assumes an exponential decaying tunneling probability from the NSQW to the surface. The passivation effect by PEALD AlN is demonstrated to last at least for months.

II. EXPERIMENT

The NSQW structures were fabricated by atmospheric pressure metalorganic vapor-phase epitaxy (MOVPE) on semi-insulating vicinal GaAs(100) substrates. Trimethylindium, trimethylgallium, and tertiarybutylarsine were used as precursors and hydrogen as the carrier gas. The nominal indium content of $In_xGa_{1-x}As$ quantum wells, $x = 0.21$, was measured by X-ray diffractometry from a reference InGaAs/GaAs multi-quantum-well sample. The nominal thicknesses of the GaAs buffer layer, the InGaAs QW, and the GaAs barrier layer were 137 nm, 4 nm and 6 nm, respectively.

The PEALD AlN layers were deposited within a day from structure growth *ex-situ* at 150, 200, and 250 °C using TMA and remote ammonia plasma (NH_3) as precursors, and nitrogen as the carrier gas. The plasma RF power was 50 W, and no pre-treatment was used before the AlN deposition. One cycle of AlN was composed of two 0.4 s TMA pulses followed by 15 s NH_3 plasma pulse. After each pulse the reactor was purged for 2, 5, and 3 s, respectively. Passivation tests by pure plasma were conducted at 150 °C where each cycle consisted only of the 15 s NH_3 plasma pulse and a 3 s purge.

PL and TRPL measurements were conducted at 30 K using standard lock-in techniques. A frequency-doubled Nd:YVO_4 laser (532 nm) was used for excitation, and a nitrogen-cooled germanium pin-diode for detection. In TRPL measurements a frequency-doubled mode-locked titanium sapphire laser operating at 400 nm was used for excitation. The pulse width was 200 fs. The TRPL signal was recorded using a micro-channel-plate photomultiplier tube combined with time-correlated photon counting electronics.

The integrated PL intensity in a steady-state condition can be expressed as[6]

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$$I = A\eta G, \tag{1}$$

where A is a constant depending, e.g., on the experimental efficiency, and G is the charge carrier generation rate due to excitation. The radiative quantum efficiency η is given by[7]

$$\eta = \frac{\frac{1}{\tau_r}}{\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}}, \tag{2}$$

where τ_r and τ_{nr} are the radiative and non-radiative carrier lifetime, respectively. Since

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}, \tag{3}$$

where τ is the carrier lifetime determined experimentally by TRPL, substituting Eqs. (2) and (3) in Eq. (1) the integrated PL intensity is given by

$$I = AG\frac{\tau}{\tau_r}. \tag{4}$$

III. RESULTS AND DISCUSSION

The optimal deposition temperature was investigated by passivating InGaAs/GaAs NSQW structures by 3–50 cycles of AlN. The PL peak position of the measured samples was 1.34 ± 0.006 eV, and the integrated PL intensities obtained from low-temperature measurements at 30 K are presented in Fig. 1. The PL readings are normalized to the so-called deep quantum well, i.e., in this case a sample with a 30-nm-thick GaAs barrier layer. The PL intensities from the unpassivated samples and samples with 50 cycles of AlN are very low and have been omitted from the figure. The highest PL intensity is observed from the sample with 20 cycles of AlN fabricated at 150 °C. The hydrogen concentration in PEALD AlN films depends on the fabrication temperature[4] and decreases with increasing temperature. A concentration of 27 at-% has been reported for layers fabricated at 150 °C. Thus, our results agree well with the results from previous studies of passivation by N_2-H_2 plasma where it has been shown that hydrogen plays a role in the passivation process.[5] Moreover, the surface roughness increases being over two times higher for samples fabricated at 300 °C than at 150 °C.[4] The deposition of 20 cycles of AlN at 150 °C results in a layer thickness of 1.5 nm and, thus, a growth rate of about 0.7 Å/cycle.

To check the repeatability of the results, another series with 0–30 cycles was fabricated at 150 °C. Furthermore, pure NH_3 plasma treatment was performed at similar conditions. The normalized integrated low-temperature PL intensities are shown (and combined with the data of Fig. 1) in Fig. 2. Details of the results of NH_3 plasma passivation are shown in the inset, since no PL was observed from samples with more than 5 cycles of plasma treatment. It is reasonable to assume that during the plasma treatment a GaN layer is formed. Thin GaN layers (~5 Å) produced by nitridation of GaAs surface by N_2-H_2 plasma have been shown to passivate the surface efficiently. Nevertheless, thicker layers lead to Fermi level pinning.[5] As shown in Fig. 2, three cycles of AlN (~2 Å) or plasma treatment enhance the PL signal. For thicker AlN layers the PL signal is enhanced even further. However, for a higher number of plasma treatment cycles the PL signal is catastrophically reduced. The highest PL intensity is achieved at 20 and 3 cycles for AlN and NH_3 plasma treatment, respectively. Comparing the intensities at these optimal cycle numbers reveals that passivation by AlN is at least four times more efficient than passivation by pure NH_3 plasma treatment. In addition, the AlN layer is amorphous and a good starting point for a high-quality HfO_2 layer for, e.g., metal-oxide-semiconductor capacitors.[8]

In addition to continuous-wave PL, the charge carrier lifetimes were measured at 30 K. The results for the AlN passivated and ammonia plasma passivated samples are plotted in Fig. 3. The lifetimes are obtained by fitting an exponentially decaying curve to the TRPL curves. This is depicted in the inset. PL intensities of InGaAs/GaAs NSQWs depend on the carrier lifetime according to Eq. (4). This model assumes that carriers can be captured by the surface states with a certain probability. This probability increases

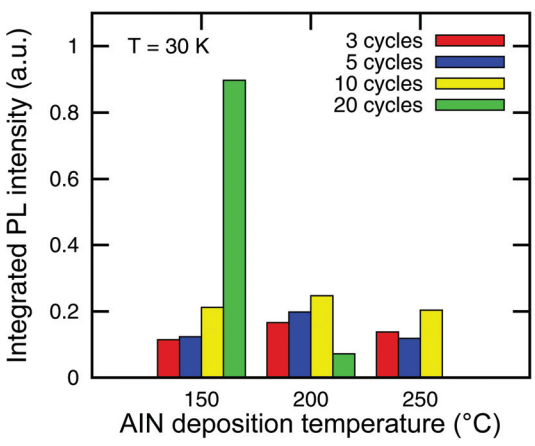

FIG. 1. Integrated PL intensities of InGaAs/GaAs NSQWs passivated by 3–20 cycles of AlN fabricated at different temperatures. The intensities have been normalized to deep QW results.

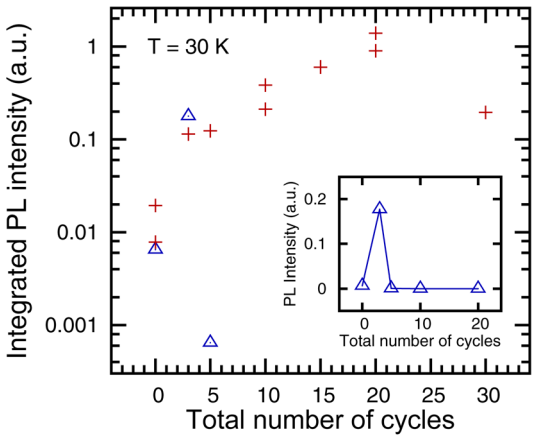

FIG. 2. Normalized integrated PL intensity of AlN passivated (+) and NH_3 passivated (Δ) NSQW structures as a function of cycles deposited. The inset shows a more detailed plot for an ammonia passivated sample. The deposition temperature was 150 °C, and the PL was measured at 30 K.

when the GaAs barrier thickness is decreased. When an InGaAs/GaAs NSQW structure is passivated, both the GaAs/AlN interface and the AlN/air surface affect the carrier behavior. When AlN is deposited, the surface state density at the GaAs interface decreases. At the same time the AlN layer grows thicker, and the distance between QW and AlN/air surface increases. Until the passivation layer reaches an optimal thickness, the carriers are captured in the surface states with a decreasing probability, which is observed as higher PL intensities and longer carrier lifetimes. This is in accordance with Eq. (4). In Fig. 3, the carrier lifetime increases until up to 20 cycles of AlN are deposited, after which it starts to decrease. The integrated PL intensity in Fig. 2 exhibited a similar trend. The charge carrier lifetime of the most efficient AlN passivation (20 cycles) is also approximately four times the charge carrier lifetime of the most efficient ammonia plasma passivation (3 cycles). All in all, the results from the lifetime measurements verify the largest reduction of surface state density when 20 cycles of AlN are deposited on a NSQW sample.

The model in Eq. (4) does not explicitly take the thickness of the passivation layer into account. However, according to PL and TRPL results, the charge carriers are captured by the surface states with decreasing probability when the AlN layer thickness is increased up to 1.5 nm (20 cycles). It is assumed that the radiative lifetime in Eq. (2) does not change with the barrier layer thickness[9] and, thus, the surface state density does not have an effect on the radiative lifetime. Therefore, the non-radiative lifetime in Eq. (2) is modeled to depend on the barrier and the passivation layer thickness. When the barrier layer thickness is kept constant, the non-radiative lifetime depends on the passivation layer thickness. It is worth mentioning that the passivation layer thicknesses here are nominal and can also be regarded as coverages. The fact that an optimal passivation layer thickness exists may indicate that the complete coverage of the GaAs surface is achieved at nominal thicknesses higher than a single monolayer of AlN. One earlier model suggests that the lifetime can be calculated from the barrier layer thickness assuming that non-radiative recombination occurs within a trapping layer determined by the occupation probability of the electrons in this layer.[9] In this model the probability is the square of the wave function integrated over the trapping layer thickness. In a simple one dimensional case the wave function in the barrier layer is exponentially decaying, and therefore, also the probability function can be expressed in the form of an exponentially decaying function. Combining this with the earlier derived model for the lifetime,[9] the charge carrier lifetime can be written using Eq. (4) as

$$\tau = \frac{\tau_r}{1 + \tau_r a \exp(-bx)} \quad , \tag{5}$$

where τ_r is the radiative lifetime, x is the AlN layer thickness, and both a and b are constants. The constant a includes the effect of the non-varying barrier layer thickness. This model is fitted to the experimental data to obtain the dashed line in Fig. 4.

According to the model the radiative lifetime saturates for large AlN layer thicknesses. That is due to the fact that the wave function approaches zero in infinity. However, in PEALD AlN passivation, a thicker layer of AlN can cause other phenomena, which are not included in the model. For example, a thick AlN layer can alter the structural properties

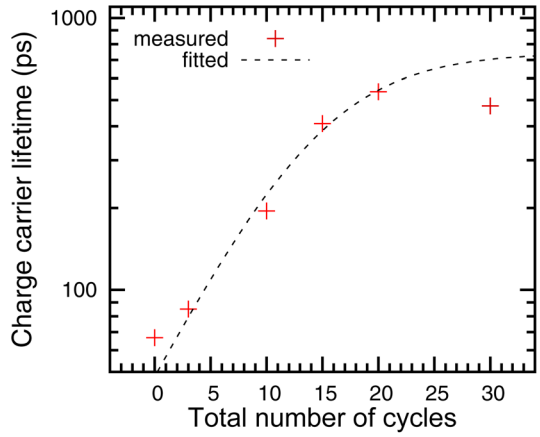

FIG. 4. Measured time constants of the AlN passivated samples and the fit according to the model in Eq. (5) as a function of the PEALD AlN cycles deposited.

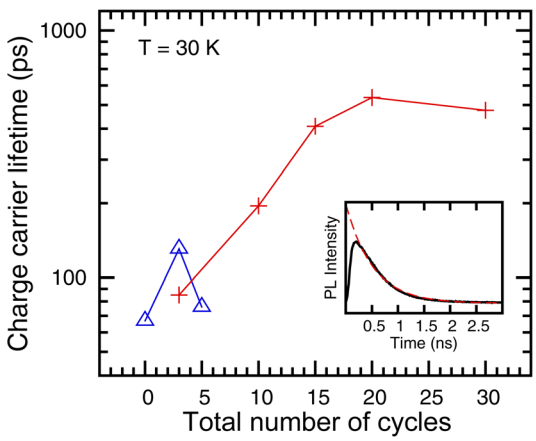

FIG. 3. Charge carrier lifetimes as a function of the cycles of AlN (+) and ammonia plasma (Δ) deposited at 150 °C. The inset shows a typical exponential fit to the measured data.

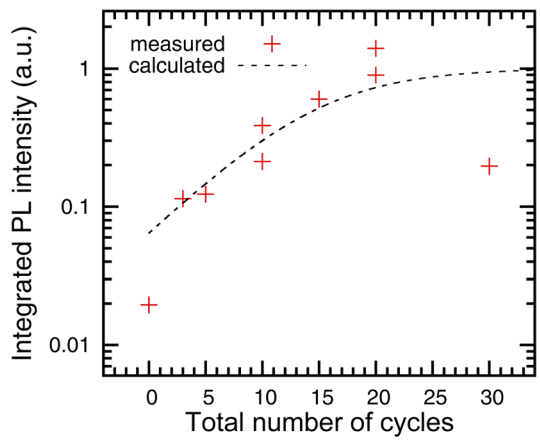

FIG. 5. Measured PL intensity and the plot of Eq. (6) as a function of AlN cycles deposited. Constants a, b, and τ_r are obtained by fitting Eq. (5) to the measured charge carrier lifetimes.

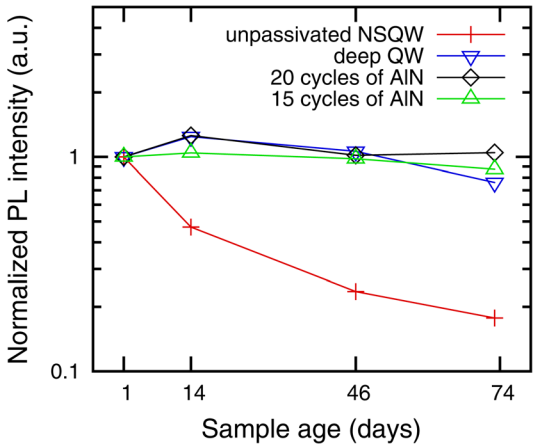

FIG. 6. Normalized PL intensity of the unpassivated NSQW, the NSQW passivated by 15 and 20 cycles of AlN, and the deep QW as a function of time. Each curve is separately normalized to start with the value of one.

of the NSQW sample or the AlN layer can trap charges.[2] This is also observed in Fig. 4, since the sample with 30 cycles of AlN clearly deviates from the fitted trend. From the fit to the data, the radiative lifetime is estimated to be 746 ps.

To model the normalized integrated PL intensity, the formula in Eq. (5) is substituted into Eq. (4). Then, the normalized integrated PL intensity has the form

$$I = \frac{1}{1 + \tau_r a \exp(-bx)}. \quad (6)$$

The constants a, b, and τ_r are obtained previously by fitting Eq. (5) to the measured lifetimes (Fig. 4). The plot of Eq. (6) is shown in Fig. 5 along with the measured PL intensity data. The model agrees well with data from samples with 3–20 cycles of AlN. The deviation with 30 cycles of AlN was already observed and explained above when the lifetimes were discussed. The PL intensity predicted by the model disagrees with the measured data from the reference sample because the model assumes a non-zero passivation layer thickness when, in fact, the reference sample is unpassivated, i.e., the passivation layer thickness is zero.

One key point in passivation is how the structure preserves its PL intensity in time. The sample passivated by 20 cycles of AlN had almost as high intensity after the growth as the deep QW. Therefore, it was measured again 14, 46, and 73 days after the fabrication. The time series is plotted in Fig. 6. For comparison, also the sample with 15 cycles of AlN, the deep QW and the unpassivated NSQW are shown. Each one of the curves is normalized separately so that the PL intensity has a value of one after the deposition. The integrated PL of the unpassivated NSQW decreases approximately to one fifth of the original value. At the same time the deep QW and the NSQW structures passivated by AlN have preserved their intensities. Therefore, it can be stated that the PEALD AlN passivation efficiency does not degrade in time.

IV. CONCLUSIONS

Surface passivation of GaAs by ammonia plasma and AlN fabricated by plasma-enhanced atomic layer deposition was investigated. Effective passivation by AlN deposited at a low temperature of 150 °C was demonstrated. The integrated PL intensity at 150 °C is four times higher than the one observed when passivation was conducted at 200 °C or 250 °C. In addition, the samples passivated by AlN had approximately four times higher PL intensities and longer PL lifetimes than the sample passivated by ammonia plasma. The optimized number of cycles was 20 (1.5 nm equivalent layer thickness) for AlN and 3 cycles for ammonia plasma. Assuming a constant radiative lifetime and a non-radiative lifetime dependent on the AlN layer thickness, a model was derived for PL intensity and charge carrier lifetime. This model explained how the PL intensity and charge carrier lifetime depend on the AlN layer thickness. Finally, the AlN passivation effect was shown to last at least for months.

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